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PROSPECTS FOR CREATING NEW OPTICALLY TRANSPARENT MATERIALS WITH YTTRIUM OXIDE AND YTTRIUM ALUMINUM GARNET (REVIEW)

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The properties of optically transparent ceramic materials made of yttrium oxide and yttrium – aluminum garnet were analyzed. The promise of preparing a transparent ceramic that combines both of these compounds was demonstrated. Methods of synthesizing yttrium oxide and yttrium – aluminum garnet were examined. Selection of the method of synthesis was substantiated. The possibility of creating such materials without modifying additives was confirmed.

Many domestic and foreign studies on creating transparent ceramic materials are currently underway, which demonstrates the demand for them in modern industry. In contrast to traditional ceramics, these materials have an almost poreless structure and can pass waves in different regions of the spectrum while retaining the other properties characteristic of ceramic materials of similar composition and in some cases, are even superior to them.

Yttrium oxide and yttrium aluminum garnet (YAG) materials have high light transmission indexes in the visible region of the spectrum. These ceramics can replace glass in instruments that operate in conditions of night vision, high temperatures, aggressive media, etc. [1].

In addition, yttrium aluminum garnet is a promising material due to the high melting point, absence of polymorphous transitions, good electrophysical indexes, stability in alkali metal plasmas, and elevated thermal stability [2]. Luminophores with the structure of garnet activated with cerium began to be used relatively recently for light-emitting diodes with white luminescence (US Patent Application No. 6744196).

Light transmission, the almost total absence of porosity, and the possibility of making products with high surface purity due to the absence of vitreous phases significantly expanded the area of application of transparent materials. For example, addition of the ionic activators Nd^{3+} (WO Patent Application No. 02/42828), Cr^{3+} (US Patent Application No. 6859480), Er^{3+} and Yb^{3+} added to ceramics [3] allows using it as the working medium for the solid-state laser.

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A relatively large amount of information has accumulated on yttrium oxide ceramics technology. Data are reported on fabrication of these materials by firing in a vacuum or hydrogen (Japanese Patent Application No. 11189413) at high temperatures, and methods of hot (RF Patent Application No. 2255071) and hot isostatic molding [4]. The method of colloidal casting is promising for creating yttrium oxide and yttrium aluminum garnet stock which is then fired in a vacuum or hydrogen [5]. However, sintering of yttrium oxide ceramics to the dense state with methods that do not require application of external effects without incorporation of ThO_2, HfO_2, La_2O_3, TiO_2 (US Patent Applications Nos. 3640887, 3545987, 4147744, and 5308809) and other modifiers is almost impossible [2].

Diffusion processes on the boundaries and in the bulk of crystals that ensure complete growth of all intracrystalline pores must actively take place to obtain poreless polycrystalline material. The rate of diffusion flows between crystals must be reduced and diffusion into their bulk must be accelerated to do this. These effects are attained in incorporating modifiers that form solid solutions with the basic oxide in the material, and the ion radius of the added oxide cation must be close to the ion radius of the basic oxide cation. Dissolved in the lattice of the basic oxide, the additive reduces the surface energy of the crystal boundaries, which decreases diffusion between boundaries and the grain growth rate. To enhance mass transfer in the crystal bulk, the cation valence of the additive and basic oxide must be different. This differences results in formation of an additional number of vacancies with respect to the cation or anion and significantly increases the pore growth rate [2].

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The use of these additives and special methods of manufacturing transparent materials is due to the increase in the cost of the final product. The presence of tetravalent cations also prevents the use of such ceramics in laser technology, since they damp the laser radiation.

Creating a material that combines the favorable properties of both yttrium oxide and yttrium aluminum garnet but contain no tetravalent modifier ions is thus promising now, as it makes it possible to use the ceramics in laser technology.

The methods of synthesizing the initial yttrium oxide and yttrium aluminum garnet powders are different. The first one can be obtained with sol-gel technology and thermal decomposition of salts, while the second is obtained by solid-phase synthesis, combustion, freezing, coprecipitation, sol-gel, and hydrothermal methods [6 – 9].

Sol-gel technology ensures production of an yttrium salt (usually nitrate or chloride), but due to the features of the technology, it is not possible to uniformly distribute it in the polymer matrix at a given time, so that synthesis of material of constant chemical composition is difficult [8]. The use of this technology for making yttrium aluminum garnet implies the use of concentrated hydrochloric acid and subsequent capture of the vapors, as well as use of complex organic reagents. All operations are conducted in a dry nitrogen atmosphere. In addition, there is an additional operation in the manufacturing process — centrifugation.

Thermal decomposition of salts is the simplest and most efficient method of obtaining monofractional yttrium oxide powder.

The precipitation method allows synthesizing homogeneous, nanosize powders with close to monofractional particle size distribution. This is possible due to the high degree of nonequilibrium of solid-phase nucleation realized when a small amount of the precipitated substance is incorporated in an excess of the precipitator. The use of viscous liquids that slow the mass-transfer diffusion and particle growth rate and reduce the probability of formation of strong aggregates is promising [10].

The combustion method makes it possible to obtain submicron yttrium aluminum garnet powders, but usually in microquantities, and synthesis of YAG is accompanied by foaming of the reaction mixture and an increase in its volume by 4 – 5 times [7].

The freezing method involves the use of hexane as a coolant and its subsequent removal with a liquid nitrogen trap and creating and maintaining low atmospheric pressure in drying for 16 – 40 h and other complicated process operations [6].

The hydrothermal method allows synthesizing 1 – 5 μm YAG particles, which does not satisfy the requirements for the initial components for manufacturing transparent ceramic materials. The use of this method for fabricating YAG involves using autoclaves for 40 – 60 h.

Solid-phase synthesis is conducted at temperatures above 1600°C. Mineralizers (usually alkaline-earth element fluorides and chlorides) are used to reduce the synthesis temperature.

The analysis of the methods of synthesizing yttrium oxide and yttrium aluminum garnet suggests that coprecipitation is the most readily implementable, since this method is simplest to implement and has long been used for production of yttrium oxide and compounds with the structure of garnet.

In precipitation from aqueous solutions, solutions of ammonium carbonate, oxalic acid, urea, and an aqueous solution of ammonia are usually used [6, 11, 12]. Synthesis of yttrium oxide by thermal decomposition of yttrium carbonate, obtained by injection spraying of a concentrated solution of yttrium chloride into a solution of ammonium carbonate in the 900 – 1500°C temperature range, is promising. Precipitation into ammonium carbonate is expedient due to the simple removal of unreacted components and production of homogeneous nanosize particles bound in loose, weak aggregates [13]. At firing temperatures above 1100°C, the wafer-like shape of the particles becomes spherical, and the characteristic size of the spheres is close to the size of the wafers [14].

The use of oxalic acid as the precipitator makes it possible to obtain yttrium oxalate with a particle size of the order of 20 – 30 μm at temperatures of 30 – 80°C [15]. It is almost impossible to synthesize transparent ceramic materials from such powders. However, decreasing the precipitation temperature reduces the particle size to 0.2 – 2.0 μm [6].

Precipitation into a solution of urea causes the formation of nitrates with a particle size of 10 – 200 nm, but in firing, the morphology of the particles is only partially changed [14]. Increasing the heat treatment temperature and time increases the cost of the final product, and this diminishes the practical value of this method.

In precipitation of basic yttrium hydroxide (precipitator: aqueous solution of ammonia), a gel-like sediment is formed which is difficult to filter and dry [16].

However, coprecipitation of hydroxides is most promising for synthesis of YAG, since they are less subject to recrystallization. Mixtures of salts, yttrium and aluminum carbonate, for example, are subject to intensive agglomeration when the usual methods of dehydration are used. The investigators in [14] partially succeeded in solving this problem — they developed a dehydration method based on azeotropic distillation of the sediment.

Our IR spectroscopic study of the initial mixture of hydroxides and the powder obtained after firing suggested the presence of bonds characteristic of yttrium aluminum garnet as early as the coprecipitation stage. This forms the basis for judging inheritance of the structural elements of precursors by the yttrium aluminum garnet crystal lattice and the possibility of obtaining a highly disperse, monofractional, and active powder with a structure close to the final product in the coprecipitation stage. This initial material allows synthesizing ceramics with a high light transmission index in the visi-

ble region of the spectrum. The hypothesis concerning inheritance of the structure is also confirmed by the data of foreign investigators [17].

The electron microscopic study of yttrium oxide and yttrium aluminum garnet powders obtained by the precipitation method confirmed the hypothesis concerning inheritance of the structure. The particle size in both cases did not exceed 400 nm.

Our studies of the properties, microstructure, and light-transmission spectra of the ceramics made from yttrium carbonate and a mixture of yttrium and aluminum hydroxides thus confirms the possibility of synthesizing a new class of optically transparent ceramic materials based on yttrium oxide and yttrium aluminum garnet in the ratio of 3 : 5 without addition of modifiers. The method of chemical coprecipitation is the most promising for making the initial raw materials since it makes it possible to synthesize nanosize powders which are homogeneous with respect to the particle size and chemical composition. This method ensures a high degree of completion of the reaction and allows obtaining YAG in the stage of synthesis of the initial powder. The advantages of the method are the comparative simplicity and absence of complicated process operations and power-consuming equipment. Using it in large-scale production will significantly reduce the cost of the final products.

Using the initial components examined opens up broad prospects for synthesis of transparent ceramic materials.

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